

Relativistic and electron correlation effects in static dipole polarizabilities for the group-14 elements from carbon to element $Z=114$: Theory and experiment

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(Received 14 July 2008; published 10 November 2008)

Static dipole polarizabilities for the 3P_0 ground state of the neutral group-14 elements C, Si, Ge, Sn, Pb and element $Z=114$ were obtained from all-electron relativistic coupled cluster theory, and compared to molecular beam electric field deflection experiments for Sn and Pb. The isotropic and anisotropic components of the polarizability increase monotonically with the nuclear charge Z , except for the spin-orbit coupled $J=0$ states, which start to decrease from Sn to Pb and even further to element $Z=114$. Hence, spin-orbit coupling leads to a significant reduction of the polarizability of element $Z=114$, i.e., from 47.9 a.u. at the scalar-relativistic Douglas-Kroll level to 31.5 a.u. at the Dirac-Coulomb level of theory, which is below the value of Si (37.3 a.u.). The calculations further demonstrate that relativistic and electron correlation effects are nonadditive. The measured dipole polarizabilities of Sn and Pb are in reasonable agreement with the theoretical values.

DOI: [10.1103/PhysRevA.78.052506](https://doi.org/10.1103/PhysRevA.78.052506)

PACS number(s): 31.15.aj, 32.60.+i, 31.15.ap, 31.15.ve

I. INTRODUCTION

The accurate determination of static dipole polarizabilities of isolated atoms or molecules currently constitutes a challenge for both experimental and theoretical research groups [1]. Recent advances on the experimental side include time-of-flight of laser cooled atoms in an electric field, which have led to a considerable improvement in the accuracy for the dipole polarizability of cesium [2]. But classical molecular beam electric field deflections methods [3–6] and interferometric techniques [7] also offer valuable information. On the theoretical side one faces the difficulty of correctly describing electron correlation and relativistic effects, as the latter increase substantially with increasing nuclear charge Z [8–14]. While closed-shell atoms and ions have been studied extensively in the past, and accurate polarizabilities are available for most of these elements, open-shell species are far more difficult to treat as often a multireference procedure is required to resolve all the $|M_L|(|M_J|)$ components of the $LS(jj)$ coupled states [1]. It is therefore not surprising that accurate polarizabilities are not easily available for open p - [15] and especially for open d - and f -shell atoms or ions [14]. For the open d - and f -shell elements one has to rely on early local density functional calculations of Doolen, who lists relativistic dipole polarizabilities [14,16,17]. Laudable exceptions are the recent paper by Fleig [18], who calculated spin-orbit resolved static polarizabilities of the group-13 atoms using four-component relativistic configuration interaction and coupled cluster methods, and the recent study of Pershina and co-workers [19], who used Dirac-Coulomb coupled cluster theory for the elements Hg, $Z=112$, Pb, and $Z=114$.

Usually, electron correlation effects to dipole polarizabilities dominate over relativistic effects for the lighter elements, as electron correlation effects can be very large [20].

In 1981 both Desclaux *et al.* [21] and Sin Fai Lam [22] demonstrated, however, that relativistic effects cannot be neglected anymore for dipole polarizabilities in heavy atoms. As an example we mention the Hg atom where relativistic effects almost halve the nonrelativistic Hartree-Fock (NRHF) value from 80 a.u. to 43 a.u. at the Dirac-Hartree-Fock (DHF) level of theory [23]. This is due to a large direct relativistic $6s$ -shell contraction. For closed p shells, relativistic effects are much less pronounced, i.e., for Rn one obtains 47.6 a.u. at the NRHF level of theory compared to 46.4 a.u. at the DHF level of theory [22]. As the spin-orbit splitting becomes very large for the heaviest p -block elements in the periodic table, we expect that such effects will considerably influence the dipole polarizabilities. In order to fill the gap for open-shell polarizabilities, we decided to undertake accurate nonrelativistic and relativistic coupled cluster calculations for all group-14 atoms in their 3P_0 ground state. Here, one has the advantage that the $p_{1/2}$ shell is complete in the jj coupled scheme. Furthermore, to the best of our knowledge there seems to be no experimental data available [24,25]. As density functional theory came under scrutiny for properties which are dependent on the long-range behavior of the density, we decided to compare our coupled cluster results to a number of well known density functional approximations. We also present experimental measurements for the dipole polarizability of both Sn and Pb using a molecular beam electric field deflection technique.

II. THEORETICAL METHODS

For the dipole polarizability calculations of the group-14 atoms we used nonrelativistic (NR), scalar-relativistic Douglas-Kroll (DK) [26–29], and Dirac-Coulomb (four-component) [30] theory within both wave-function-based methods (Hartree-Fock(HF), second-order many-body per-

turbation theory for the electron correlation, second-order Moller-Plesset model (MP2), and coupled cluster singles-doubles including perturbative triples [CCSD(T)], and density functional theory (the local density functional approximation (LDA) [31], the generalized gradient approximations (GGA) Perdew-Burke-Ernzerhof (functional) (PBE) [32] and BLYP [33], and the hybrid functional Becke three-parameter Lee-Yang-Parr (B3LYP) [34,35]). In the Dirac picture, Kramers (time-reversal) symmetry was applied in the coupled cluster procedure [KRCCSD(T)] to save computer time [36]. If analytical procedures were not available for the calculation of the polarizability tensor, we used a finite field method instead. In this case fields of 0.0, 0.001, 0.002, and 0.005 a.u. were applied. In the nonrelativistic and scalar relativistic cases the two tensor components of $M_L=0$ and $M_L = \pm 1$ were obtained in the finite field method by fixing the occupation of the p orbitals lying parallel or perpendicular to the homogeneous electric field applied. For the open-shell procedure we used spin unrestricted Hartree-Fock and Kohn-Sham theory. We applied extensive, uncontracted Gaussian-type basis sets, which were thoroughly tested to yield converged polarizabilities with respect to basis set extension towards softer and harder functions at the coupled cluster level. In detail, we started from uncontracted, augmented correlation consistent quadruple-zeta basis sets (aug-cc-pVQZ) [37–39] and derived at $(13s/7p/4d/3f/2g)$ for C, $(17s/12p/4d/3f/2g)$ for Si, and $(23s/19p/15d/4f/2g)$ for Ge. For these elements we used the full active orbital space in our electron correlation procedure. For Sn we used an extended dual-type Dyal-QZ basis set [40], and added a soft $(3s/2p/3d/6f/2g)$ set of functions to end up with a $(36s/29p/21d/6f/2g)$ basis set. We correlated all orbitals between -12 a.u. and $+100$ a.u. (22 electrons). Similarly, for Pb starting with the original Dyal-QZ set [40] we derived a $(37s/33p/25d/19f/2g)$ basis set by adding a soft $(3s/2p/4d/5f/2g)$ set. Here, we correlated all orbitals between -10 a.u. and $+100$ a.u. (36 electrons). Finally, for element 114 ($Z=114$) we used the Faegri basis set [41] as a starting point and ended up with a decontracted $(32s/31p/24d/18f/3g)$ set of Gaussian functions. Here we correlated orbitals between -7 a.u. and $+100$ a.u. (36 electrons). Finally, we considered the Gaunt term. In the Feynman gauge, the interaction between two electrons i and j becomes [42]

$$V_G(r_{ij}, \omega_{ij}) = r_{ij}^{-1} (1 - \vec{\alpha}_i \cdot \vec{\alpha}_j) e^{ic^{-1}|\omega_{ij}|r_{ij}}. \quad (1)$$

Since the frequency of the virtual exchange photon ω_{ij} is small compared to c/r_{ij} (c is the velocity of light), the frequency dependent exponential is neglected in our calculation (low frequency limit). Perdew and Cole implemented the Breit term within a local density approximation, but pointed out that accurate ionization potentials can only be achieved by including the self-interaction term in DFT [43]. We therefore decided to evaluate the Gaunt interaction to the polarizability at the Dirac-Hartree-Fock level of theory only.

At the nonrelativistic and scalar-relativistic level of theory we define the (state) average polarizability $\bar{\alpha}$ and anisotropy $\Delta\alpha$ of the polarizability tensor for the $L=1$ state as

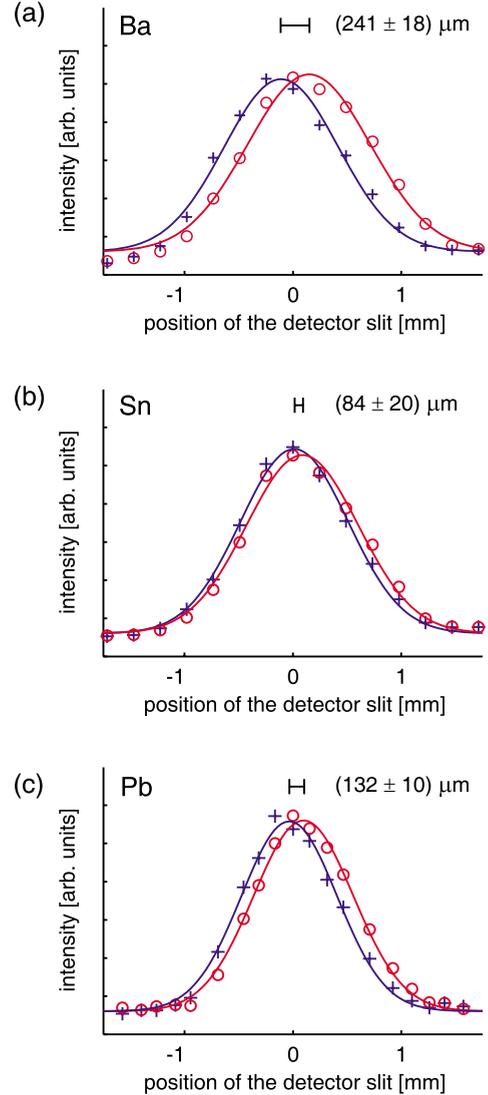


FIG. 1. (Color online) Molecular beam profiles of Ba (a) [5], Sn (b), and Pb (c) atoms with (circles) and without (crosses) applied electric deflection field. As a guide to the eye the experimental beam profiles are fitted with Gaussian functions. The field-induced beam deflections d are indicated above the profiles.

$$\bar{\alpha} = (\alpha_0 + 2\alpha_1)/3, \quad (2)$$

$$\Delta\alpha = \alpha_1 - \alpha_0, \quad (3)$$

where α_0 and α_1 are the polarizability components for $M_L=0$ and $M_L = \pm 1$, respectively.

III. EXPERIMENTAL METHOD

The polarizabilities α of tin and lead atoms are experimentally determined utilizing a molecular beam electric field deflection apparatus, previously described in the literature [5]. Short, pulsed molecular beams of tin and lead atoms are generated with a laser ablation source using tin and lead targets. The laser ablation source is equipped with a temperature-controlled, cryogenic vacuum expansion nozzle,

which offers the possibility to produce slow atomic ground state species in the molecular beam. In our experiments on tin atoms, the nozzle was held at 100 K, in the case of lead atoms at 40 K. After the expansion the molecular beam is tightly collimated and passed through an inhomogeneous electric field, where it gets deflected. The deflection d is measured by scanning a movable slit across the molecular beam profile and detecting transmitted atoms with a time-of-flight mass spectrometer. For this purpose the atoms are ionized with a F_2 -excimer laser. The deflection d of the molecular beam is related to the polarizability α by

$$d = \frac{A}{mv^2} \alpha, \quad (4)$$

with an apparatus constant A , the mean velocity v of the particles, which is measured with a molecular beam shutter, and the mass m of the atoms. If several stable isotopes of an atom exist, $1/m$ has to be replaced by the weighted mean $\langle 1/m \rangle$ of the inverse masses of these isotopes. However, $\langle 1/m \rangle$ differs by less than 1% from $1/\langle m \rangle$ for tin and lead. We therefore used the latter in our analysis of the experimental data.

By comparing the deflection of, e.g., lead d_{Pb} to the beam deflection of a species with known polarizability, as barium [5,44], the absolute value of the polarizability α_{Pb} is given by

$$\alpha_{\text{Pb}} = \alpha_{\text{Ba}} \frac{d_{\text{Pb}} m_{\text{Pb}} v_{\text{Pb}}^2}{d_{\text{Ba}} m_{\text{Ba}} v_{\text{Ba}}^2}. \quad (5)$$

With the current apparatus it is not possible to measure the polarizability of the lighter homologues of tin and lead, since the ionization potentials of carbon (11.26 eV), silicon (8.15 eV), and germanium (7.90 eV) [45] exceed the energy per photon of the ionization laser (7.87 eV).

IV. RESULTS AND DISCUSSION

The molecular beam profiles with and without electric deflection field of tin and lead atoms are shown in Fig. 1 in comparison to the beam deflection of barium atoms, which is used as a calibrant [5]. The mean velocity of tin, lead, and barium atoms was determined to be 1020, 650, and 1410 m/s, respectively, with an accuracy of 2%. Using Eq. (5) and the experimental polarizability of the barium atom $\alpha_{\text{Ba}} = (268 \pm 21)$ a.u. [44], the polarizabilities of tin $\alpha_{\text{Sn}} = (42.4 \pm 11)$ a.u. and lead $\alpha_{\text{Pb}} = (47.1 \pm 7)$ a.u. are obtained. The error margins in the case of tin are significantly enlarged compared to lead, since it was not possible to generate a sufficiently intense molecular beam of tin atoms at expansion nozzle temperatures below 100 K. This leads to the higher velocities of the tin atoms and thereby reduced deflections in the electric field.

The results of all calculations are summarized in Table I. The most accurate coupled cluster results including the Gaunt term at the DHF level are compared to other theoretical data in Table II. There is excellent agreement of our results with the nonrelativistic CCSD(T) value of carbon and silicon obtained by Thakkar and co-workers [48,49]. These authors also provide a more complete overview of previous

results. The anisotropy $\Delta\alpha$ for carbon and silicon of Thakkar and co-workers are 2.10 and 8.41 a.u., respectively, which are also in excellent agreement with our nonrelativistic results (2.13 and 8.57 a.u.). Further, very recent results at the Dirac-Coulomb level of theory for the heaviest elements Pb and $Z=114$ from Pershina and co-workers [19] also agree with ours. This gives us confidence for the accuracy of all our results.

Figure 2 compares the calculated polarizabilities at the HF and CCSD(T) level of theory. Relativistic and electron correlation effects are shown in Fig. 3 and in Table II. We make the following observations: (i) At the nonrelativistic and scalar-relativistic levels, both the polarizability $\bar{\alpha}$ and the anisotropy $\Delta\alpha$ increase with increasing nuclear charge of the group 14 element. (ii) From a comparison between nonrelativistic and scalar-relativistic polarizabilities we obtain a roughly Z^2 increase in relativistic effects for the $M_L=0$ component, while there is little change for the $M_L=\pm 1$ component of the polarizability tensor. (iii) The anisotropies are larger at the scalar relativistic level compared to the nonrelativistic results, in fact, the relativistic change in the anisotropies roughly increase with Z^2 . (iv) Electron correlation reduces the dipole polarizability (with the exception of the $J=0$ state for element $Z=114$) by about 1 (C) to 6 ($Z=114$) a.u., but is much less pronounced compared to the dipole polarizabilities of the s -block elements [12,13,19]. (v) For the lighter elements, LS coupling (spin-orbit coupling small) gives a much better description than jj coupling. Hence, it is of no surprise that the relativistic Hartree-Fock wave function, with the $p_{1/2}$ doubly occupied, is not the best zero-order wave function for the electron correlation procedure as the lowest energy field perturbation in the LS -coupled $M_L=\pm 1$ state. Thus, to compensate for this the coupled cluster procedure leads to a larger correlation effect in the jj -coupled case compared to the LS -coupled case for elements where spin-orbit interactions can be neglected. In contrast to the HF case, the polarizabilities for the Dirac $J=0$ and Douglas-Kroll $M_L=\pm 1$ state agree nicely at the coupled cluster level for carbon. (vi) Figure 3 clearly shows that spin-orbit contributions are as important as scalar relativistic effects for these p -block elements, and that they are not even negligible for carbon. (vii) Already for Ge, relativistic effects (including spin-orbit) are as important as electron correlation. For element $Z=114$ we see a huge reduction in the dipole polarizability (64%) from 88.0 to 31.5 a.u. due to relativistic effects. As a result, element $Z=114$ has a smaller dipole polarizability compared to Si (37.3 a.u.), as discussed in detail by Pershina *et al.* [19]. Pershina and co-workers also pointed out that the polarizability nicely correlates with the mean radius of the $p_{1/2}$ orbital. (viii) The Gaunt contribution increases with nuclear charge and, for the three heaviest elements, cannot be neglected anymore in precise calculations. (ix) Correlating the next shell below the $nsnp$ -valence shell is also important. For example, we see a change from 37.47 to 37.28 a.u. for Si and from 47.68 to 47.34 a.u. for Pb due to core correlation. (x) Triple contributions to the CCSD procedure are rather small, indicating that higher (quadruple) contributions are probably negligible. (xi) Finally, the results clearly show that relativistic and electron correlation effects are nonadditive.

TABLE I. The static dipole polarizabilities (in a.u.) of the group-14 elements at different levels of theory. Nonrelativistic (NR) and scalar-relativistic Douglas-Kroll (DK) calculations are for the $M_L=0$ and $M_L = \pm 1$ components of the 3P state, and Dirac values are for the $J=0$ state.

| | NR (3P) | | | DK (3P) | | | Dirac $J=0$ $M_J=0$ |
|-----------|--------------|-------------|---------|--------------|-------------|---------|------------------------|
| | $M_L=0$ | $M_L=\pm 1$ | Average | $M_L=0$ | $M_L=\pm 1$ | Average | |
| Carbon | | | | | | | |
| HF | 10.91 | 12.51 | 11.97 | 10.89 | 12.50 | 11.96 | 11.76 |
| LDA | 11.39 | 14.18 | 13.25 | 11.38 | 14.18 | 13.25 | 14.28 |
| PBE | 11.42 | 14.50 | 13.48 | 11.42 | 14.51 | 13.48 | 14.30 |
| BLYP | 11.44 | 14.42 | 13.42 | 11.43 | 14.42 | 13.42 | 14.44 |
| B3LYP | 11.05 | 13.55 | 12.72 | 11.04 | 13.55 | 12.71 | 13.52 |
| MP2 | 9.64 | 12.31 | 11.42 | 9.64 | 12.31 | 11.42 | 12.06 |
| CCSD | 10.21 | 12.33 | 11.63 | 10.20 | 12.33 | 11.62 | 11.34 |
| CCSD(T) | 10.28 | 12.41 | 11.70 | 10.27 | 12.41 | 11.70 | 11.26 |
| Silicon | | | | | | | |
| HF | 32.56 | 41.39 | 38.45 | 32.48 | 41.46 | 38.46 | 41.66 |
| LDA | 33.71 | 45.48 | 41.56 | 33.67 | 45.63 | 41.64 | 44.95 |
| PBE | 34.00 | 45.53 | 41.68 | 33.95 | 45.66 | 41.76 | 44.93 |
| BLYP | 34.46 | 46.79 | 42.68 | 34.42 | 46.94 | 42.77 | 46.37 |
| B3LYP | 33.44 | 44.33 | 40.70 | 33.39 | 44.45 | 40.76 | 44.09 |
| MP2 | 32.02 | 40.68 | 37.79 | 31.97 | 40.76 | 37.83 | 40.73 |
| CCSD | 31.76 | 40.31 | 37.46 | 31.70 | 40.39 | 37.49 | 37.69 |
| CCSD(T) | 31.83 | 40.40 | 37.54 | 31.77 | 40.58 | 37.58 | 37.28 |
| Germanium | | | | | | | |
| HF | 34.02 | 45.26 | 41.51 | 33.24 | 45.30 | 41.28 | 43.86 |
| LDA | 34.14 | 49.18 | 44.17 | 33.59 | 49.63 | 44.29 | 46.23 |
| PBE | 35.29 | 50.60 | 45.49 | 34.73 | 51.09 | 45.64 | 47.92 |
| BLYP | 35.59 | 51.81 | 46.40 | 35.07 | 52.32 | 46.57 | 48.61 |
| B3LYP | 34.39 | 48.60 | 43.86 | 33.78 | 48.96 | 43.91 | 45.94 |
| MP2 | 32.66 | 43.43 | 39.84 | 31.93 | 43.47 | 39.63 | 41.70 |
| CCSD | 32.82 | 43.78 | 40.13 | 32.11 | 43.84 | 39.93 | 39.94 |
| CCSD(T) | 32.83 | 43.83 | 40.16 | 32.11 | 43.90 | 39.97 | 39.33 |
| Tin | | | | | | | |
| HF | 50.69 | 63.09 | 58.96 | 47.17 | 62.34 | 57.28 | 57.35 |
| LDA | 48.60 | 65.12 | 59.61 | 46.21 | 65.74 | 59.23 | 57.45 |
| PBE | 50.87 | 68.06 | 62.33 | 48.41 | 68.90 | 62.07 | 60.44 |
| BLYP | 51.06 | 69.44 | 63.31 | 48.76 | 70.29 | 63.11 | 60.80 |
| B3LYP | 49.67 | 65.51 | 60.23 | 47.05 | 65.90 | 59.62 | 58.01 |
| MP2 | 45.88 | 59.53 | 54.98 | 43.58 | 59.79 | 54.39 | 54.25 |
| CCSD | 47.74 | 60.68 | 56.37 | 44.81 | 60.53 | 55.29 | 53.32 |
| CCSD(T) | 47.63 | 60.70 | 56.34 | 44.74 | 60.60 | 55.31 | 52.70 |
| Lead | | | | | | | |
| HF | 58.42 | 72.04 | 67.52 | 46.87 | 70.10 | 62.36 | 49.71 |
| LDA | 55.01 | 73.17 | 67.00 | 47.24 | 74.59 | 65.47 | 49.86 |
| PBE | 57.83 | 76.85 | 70.53 | 49.77 | 79.25 | 69.42 | 52.81 |
| BLYP | 58.01 | 77.89 | 71.46 | 50.45 | 80.34 | 70.37 | 53.05 |
| B3LYP | 56.46 | 73.88 | 68.09 | 48.02 | 74.82 | 65.89 | 50.48 |
| MP2 | 51.75 | 66.77 | 61.76 | 43.65 | 67.30 | 59.42 | 47.63 |

TABLE I. (Continued.)

| | NR (3P) | | | DK (3P) | | | Dirac $J=0$ $M_J=0$ |
|-----------------|--------------|-------------|---------|--------------|-------------|---------|------------------------|
| | $M_L=0$ | $M_L=\pm 1$ | Average | $M_L=0$ | $M_L=\pm 1$ | Average | |
| CCSD | 54.56 | 68.71 | 63.99 | 44.69 | 67.97 | 60.21 | 47.36 |
| CCSD(T) | 54.36 | 68.66 | 63.90 | 44.67 | 68.04 | 60.25 | 47.34 |
| Element $Z=114$ | | | | | | | |
| HF | 76.75 | 91.18 | 86.39 | 49.69 | 101.40 | 84.16 | 30.13 |
| LDA | 70.27 | 88.92 | 82.70 | 52.31 | 98.37 | 83.02 | 33.34 |
| PBE | 75.18 | 96.83 | 89.61 | 56.17 | 109.14 | 91.48 | 34.17 |
| BLYP | 74.59 | 96.37 | 89.11 | 57.07 | 107.08 | 90.42 | 35.35 |
| B3LYP | 72.84 | 91.54 | 85.31 | 53.36 | 101.10 | 85.19 | 33.08 |
| MP2 | 65.05 | 92.09 | 78.64 | 47.26 | 93.64 | 78.18 | 32.02 |
| CCSD | 70.92 | 88.25 | 82.47 | 47.88 | 94.97 | 79.28 | 31.05 |
| CCSD(T) | 70.29 | 88.04 | 82.12 | 47.90 | 94.66 | 79.07 | 31.49 |

We next ask if some of the popular density functionals are able to accurately reproduce dipole polarizabilities for these p -block elements. There are some notable failures in the past. For example, Stott and Zaremba [46] reported a LDA value of 1.89 a.u. for He, far too high compared to the experimental value of 1.3832 a.u. [47]. More recent calculations with larger basis sets and a variety of different functionals give a better comparison, i.e., one obtains 1.686 ($X\alpha$), 1.644 (LDA), 1.558 [the Becke-Perdew-Wang GGA functional (BPW91)], and 1.505 [the hybrid functional (B3LYP)] a.u., in comparison to wave-function-based methods, 1.322 (HF) and 1.362 (MP2) a.u. [14]. In our case, all functionals overestimate the dipole polarizability by a few atomic units. Increasing the exact exchange will not help as the HF value is larger than the coupled cluster value. Instead one needs to correct for the wrong long-range behavior in common density functionals. We note that the overestimation is proportional to the polarizability, that is, the worst DFT results are

obtained for the Sn atom, which exhibits the highest polarizability of all group-14 elements. The recommended polarizabilities for all group-14 elements for the lowest 3P_0 state are listed in Table II. For Pb and element $Z=114$ Pershina *et al.* [19] took slightly different basis sets including h functions. As their values are slightly smaller compared to ours, we list theirs, however, correcting them with our calculated Gaunt contribution.

Comparing the experimentally determined polarizabilities of Sn and Pb with the theoretical predictions in Table I, it is obvious, especially in the case of Pb, that not only the scalar-relativistic but also the spin-orbit correction has to be taken into account, in order to reproduce the experimental data. Hence, most of the atoms in the beam are in the $J=0$ ground state, as one expects for such large spin-orbit splittings and low temperatures. However, the large error margins of the experimental polarizabilities expresses the need

TABLE II. Total relativistic, Δ_R , including spin-orbit corrections for the 3P_0 state (relative to the $M_L = \pm 1$ component). Gaunt, Δ_{Gaunt} , at the DHF level of theory and electron correlation contributions, Δ_{corr} , for the $J=0$ state, and final Gaunt-corrected KR-CCSD(T) for the dipole polarizabilities of the group-14 elements compared to previous theoretical results. All values are in a.u. The recommended values are from our CCSD(T) results and from Pershina *et al.* [19], and corrected for Gaunt interactions.

| Method | C | Si | Ge | Sn | Pb | $Z=114$ |
|------------------------------|--------------------|--------------------|-------------------|-------------------|--------------------|--------------------|
| Δ_R | -1.15 | -3.12 | -4.50 | -8.27 | -21.33 | -56.55 |
| Δ_{Gaunt} | 0.005 | 0.032 | 0.097 | 0.21 | 0.37 | 0.38 |
| Δ_{corr} | -0.50 | -4.38 | -4.53 | -4.65 | -2.37 | 1.18 |
| KR-CCSD(T)+ Δ_{Gaunt} | 11.26 | 37.31 | 39.43 | 52.91 | 47.70 | 31.87 |
| Others | 11.67 ^a | 37.17 ^b | 41.0 ^c | 52.0 ^d | 46.96 ^e | 30.59 ^e |
| Recommended | 11.3 | 37.3 | 39.4 | 52.9 | 47.3 | 31.0 |
| Experimental | | | | 42.4 \pm 11 | 47.1 \pm 7 | |

^a $\bar{\alpha}$ NR-CCSD(T) taken from Ref. [48].

^b $\bar{\alpha}$ NR-CCSD(T) taken from Ref. [49].

^c $\bar{\alpha}$ NR-PNO-CEPA taken from Ref. [50].

^dR-LDA taken from Refs. [16,17].

^eDirac-Coulomb CCSD(T) results for $J=0$ taken from Ref. [19].

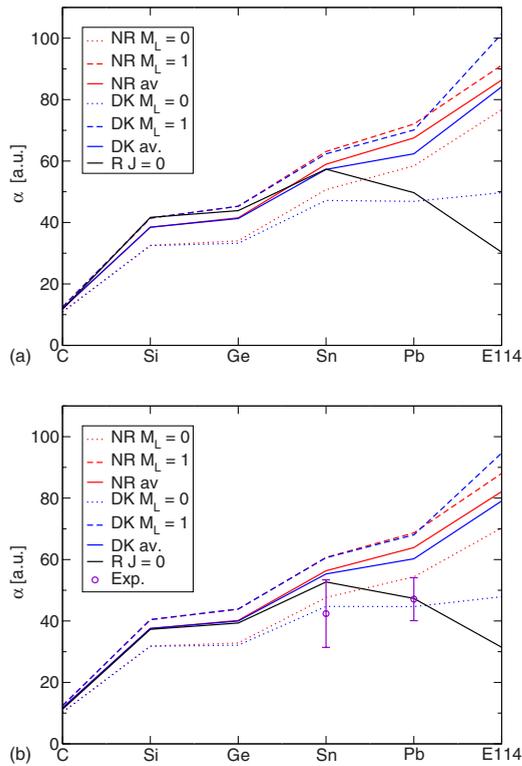


FIG. 2. (Color online) The static dipole polarizabilities of the group-14 elements at the HF (upper picture) and CCSD(T) (lower picture) level of theory. Nonrelativistic (NR) and scalar-relativistic Douglas-Kroll (DK) calculations are for the $M_L=0$ and $M_L=\pm 1$ components of the 3P state, and Dirac values are for the $J=0$ state. Experimental values for Sn and Pb are given with error bars.

for future high-precision experiments to actually check the accuracy of theoretically predicted polarizabilities of the open-shell atoms discussed in this work. Also, more work has to be done on other open p -, as well as the open d - and f -shell elements, and in our case, for the energetically higher lying $J=1$ and 2 states, which requires a multireference procedure.

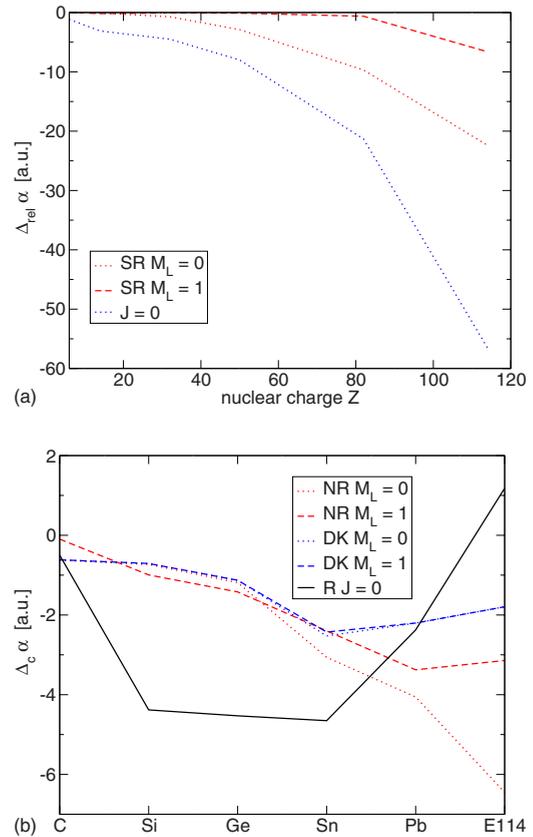


FIG. 3. (Color online) Relativistic (upper picture) and electron correlation (lower picture) effects for the $M_L=0$ and $M_L=\pm 1$ components of the 3P state, and for the Dirac $J=0$ state (see Table II for details).

ACKNOWLEDGMENTS

This work was financed by a Marsden grant (Grant No. 06-MAU-057) through the Royal Society of New Zealand and the Deutsche Forschungsgemeinschaft by Grant No. SCHA885/7-1. Sascha Schäfer acknowledges support from Fonds der Chemischen Industrie. We thank Daniel Benker for helpful discussions.

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